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The effects of concentration polarization on electrodeposition with controlled cathode potential

Eugene Merridith Sallee
Iowa State College

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**THE EFFECTS OF CONCENTRATION POLARIZATION
ON ELECTRODEPOSITION WITH CONTROLLED
CATHODE POTENTIAL**

by

Eugene Merridith Sallee

**A Thesis Submitted to the Graduate Faculty
for the Degree of**

DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

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I. INTRODUCTION

Chemical analysis by electrodeposition is normally accomplished by passing a current between inert electrodes in a solution containing metal ions. The metal being determined is deposited at the cathode or in some cases (Pb and Mn) as the oxide at the anode. The reversible or equilibrium potential between a metal and its ions depends on the activity of the ions in solution and the standard reference potential for the reaction. This equilibrium potential can be calculated for the general reaction, $M^{+n} + n e \rightleftharpoons M^0$, by using Nernst's equation, $E = E^0 + \frac{RT}{nF} \ln[M^{+n}]$ for any activity of the metallic ions. As a deposition progresses the activity of the ion decreases and the potential increases until another metal, if present, or hydrogen is deposited. To insure complete deposition of a desired metal without these interfering reactions it is necessary to reduce the applied voltage from time to time to limit the cathode-solution potential. Recently apparatuses for the automatic control of the cathode potential during an electrodeposition have been described by Hickling (16), by Caldwell, Parker, and Diehl (5), and by Lingane (24).

To use such an apparatus it is necessary to determine in some way the correct limiting potential for given conditions. With the passage of a current through a solution, equilibrium conditions are not maintained and the potential difference

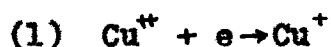
between the electrodes is greater than that predicted by Nernst's equation. The difference in potential between the reversible and the actual values to pass a current is called overvoltage. Overvoltage, though most commonly considered when gases are being discharged at the electrodes, applies equally well to the deposition of metals. The overvoltage includes the IR drop between the electrodes, an activation potential, and polarization effects. In the solution of strong electrolytes normally used in electrodeposition the resistance is small, and when the cathode-solution potential is measured with a potentiometer, the current flow in the measuring circuit is so low that this IR drop is negligible. The so called activation potential for depositing metal on metal of similar crystal structure and spacing is also quite small, however, in early stages it may be large due to dissimilarities in the structure of the metals involved. It is this activation potential which causes the "super-saturation" effects described by Erdey-Grúz and Volmer (9). Polarization, on the other hand, may be more than 0.1 volt.

Even with vigorous stirring a film of solution adheres to the electrode, and ions removed from this film by electrolysis must be replenished by diffusion. Since the potential depends on the activity of the ions in the solution in contact with the metal and since during passage of current this is always less than of the solution as a whole, the

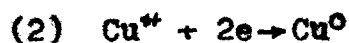
metal-solution potential is abnormally large. The phenomenon just described is concentration polarization. Another type of polarization, chemical polarization, may also be involved. Little is known about the exact nature of chemical polarization but it involves the formation of a chemical compound or complex at the electrode surface. Concentration polarization, resulting as it does from the depletion of the ions in the electrode layer, is dependent on conditions. Increased rate of stirring and higher temperatures decrease and higher current densities increase concentration polarization.

The present investigation was undertaken with the purpose of determining the magnitude of concentration polarization in the deposition of copper from an acid chloride solution so that the correct limiting potential to be used for a deposition could be calculated. Copper was chosen because of its commercial importance and because previous work has been done in this laboratory with copper and its alloys.

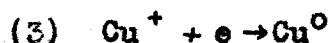
During the electrolysis of solutions of copper, three reactions with corresponding potentials are possible:



$$E_{\text{Cu}^{++}, \text{Cu}^+} = 0.167 + .059 \log \frac{[\text{Cu}^{++}]}{[\text{Cu}^+]} \quad (\text{at } 25^\circ\text{C})$$



$$E_{\text{Cu}^{++}, \text{Cu}^0} = 0.3448 + \frac{.059}{2} \log [\text{Cu}^{++}]$$



$$E_{\text{Cu}^+, \text{Cu}^0} = 0.522 + .059 \log [\text{Cu}^+]$$

The E^0 values in the above equations were taken from Latimer (19). As in any case where two valence states exist for an ion, the reversible E for the higher valence state is between that for the reduction and that for the lower valence state (except when all three are equal). That is, $E_{\text{Cu}^+, \text{Cu}^0}$ is greater than $E_{\text{Cu}^{++}, \text{Cu}^0}$ is greater than $E_{\text{Cu}^{++}, \text{Cu}^+}$ or $E_{\text{Cu}^+, \text{Cu}^0}$ is less than $E_{\text{Cu}^{++}, \text{Cu}^0}$ is less than $E_{\text{Cu}^{++}, \text{Cu}^+}$. In sulfate or nitrate solutions the former holds but the cuprous concentration is extremely low so the deposition principally proceeds according to equation (2) above. In chloride solutions, however, a complex anion, CuCl_3^- , is formed if the total chloride concentration is greater than 0.4 molar. The instability constant of this anion was calculated by Diehl and Brouns (7) from solubility data in the literature as 1.23×10^{-6} in 1 molar potassium chloride. The formation of this complex ion greatly reduces the cuprous concentration and thus $E_{\text{Cu}^+, \text{Cu}^0}$ is decreased and $E_{\text{Cu}^{++}, \text{Cu}^+}$ is increased so that the latter is the higher potential and the reaction during early stages of an electrolysis is reduction of cupric ions, and, though current is carried by the solution, no copper is deposited. This reduction continues until the cuprous and cupric activities are such that when substituted in the above equations $E_{\text{Cu}^+, \text{Cu}^0}$ is greater than $E_{\text{Cu}^{++}, \text{Cu}^+}$ and deposition begins. Most of the

univalent copper in chloride solutions is in the form of complex anions and reactions (1) and (3) could equally well be considered as involving chlorocuprous rather than cuprous ions. The instability constant for the anion would then be included in the E^0 values. The form used was chosen to avoid introducing a calculated constant in the potential equations. The actual electrode reactions are discussed in Section IV A.

It should be noted that here, as in the case of the copper-ammonia complex studied by Newton and Furman (27), the initial reduction is hindered by high copper content and efficient stirring. The better the stirring, the more likely cuprous is to be air oxidized, and the higher the total copper concentration, the more current must be passed to effect the preliminary reduction. Thus, paradoxically, the more copper present and the more efficient the stirring the more difficult it is to start and maintain the deposition.

II. REVIEW OF THE LITERATURE

The problem of concentration polarization has been attacked principally in two ways. Composition of the boundary layer at the electrode has been studied, and direct measurement of the polarization has been accomplished by plotting current density--potential curves and extrapolating to zero current.

Brenner (2) determined experimentally the concentration difference between the boundary layer and the main body of copper solutions by both freezing and wiping methods. In the former method, he used a hollow cylinder as cathode and after establishing equilibrium (at current density of .02 amps/cm²) filled it with a pre-cooled liquid. By using a lathe the resulting coating of ice was then cut from the cathode in layers for analysis. In the wiping method a plane cathode was used and after draining for three seconds the remaining liquid was removed with a squeegee and analyzed. Results indicated a cathode film of from .010 to .012 inches in thickness and a concentration in the film 0.75 N less than the 2 N copper sulfate in the body of the solution. Neither of these methods can be used for a gauze electrode.

A different approach to the problem was made by Levich (21) who developed an expression for calculating the maximum current (with 100% efficiency) from considerations of hydrodynamics and geometry of the electrodes. Kasper (18) discussed

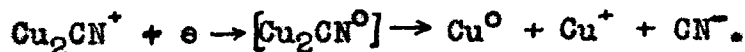
the theory of potential between various shaped electrodes in a series of papers. The ideal conditions used in these developments could scarcely be attained in practice and it is not possible to determine by calculation the hydrodynamics for a platinum gauze cylinder of the type commonly used for analysis by electrodeposition. Of more practical value to the present investigation were the experimental determinations of polarization.

By plotting current density against potential, an experimental estimation of the polarization can be made; the potential at zero current being considered equilibrium and the difference between that and the measured value, the polarization. This is possible because the IR drop in the potential measuring circuit is negligibly small and the activation potential for a given electrode reaction, both small and constant.

Cathode polarization of cuprous solutions has been studied in a number of solutions containing complex ions. Because of their importance as commercial plating baths, cyanide solutions have received considerable attention. A thorough experimental study of electrodeposition from cyanide solutions was made by Glasstone (13) who studied a number of metals. His work with silver and copper is particularly interesting from the point of view of the present investigation. By determining current efficiency in conjunction with current density--potential measurements, Glasstone determined the

current density at which a second reaction begins. This reaction is probably the simultaneous discharge of hydrogen but in cyanide solutions this is by no means certain since methylamine may be formed at the cathode. In chloride solutions the deposition of gaseous hydrogen is probable. In a stirred solution of 0.1 N potassium cyanide saturated with cuprous cyanide a second reaction began to reduce the efficiency between 1.5 and 2.5 milliamps/cm².

In attempting to explain the smooth, fine-grained deposits obtained with these solutions of complex ions Glasstone presented an interesting speculation. He suggested the existence of complex cations of the type Ag_2CN^+ and Cu_2CN^+ , the deposition taking place by the reaction,



In support of this hypothesis Glazunov, Starosta, and Vondrasek (14) present photographs purporting to prove the deposition of copper from a cyanide bath on glass fibers attached to the cathode. Unfortunately their experimental details were not reported and the present work makes it appear that their photographs may have been misinterpreted. No other attempts to prove or disprove Glasstone's suggestion have been found.

Newton and Furman (27) reported a study of copper potentials and polarization in deposition from ammoniacal solutions in 1942. Their depositions were carried out at constant cur-

rent with no attempt to limit the copper cathode--solution potential. Near the end of the deposition the potential of an auxilliary copper electrode decreased in a period of about 30 minutes by 0.2 volt. Though Newton and Furman apparently did not realize it, this decrease is particularly significant since Brown (4) suggested limiting the potential between cathode and an auxilliary electrode as a means of separating metals and since it is common practice to consider that an auxilliary electrode of the metal being deposited measures the equilibrium potential.

Based on a study of complex thiocyanate solutions Philbert (28) concluded that there was no "overvoltage" in the initial reduction and that if any existed in the deposition reaction, $\text{Cu}^+ + e \rightarrow \text{Cu}^0$, it was certainly slight.

The deposition of copper from halide solutions has also been studied by many investigators. Thon and Pinilla (29) in 1932 presented an unusual mechanism for deposition of copper from halide solutions. They contended that the plateau in the current density--potential curves for copper in complex solutions (see Fig. 6) was due to two different electrode reactions. At very low current density (according to Thon and Pinilla) the current is carried by the reduction, $\text{Cu}^{++} + e \rightarrow \text{Cu}^+$, and the deposition accomplished by the chemical reaction, $2\text{Cu}^+ \rightleftharpoons \text{Cu}^0 + \text{Cu}^{++}$. At higher current densities the reaction is $\text{Cu}^+ + e \rightarrow \text{Cu}^0$. They extrapolated the two

branches of the curve to zero current and measured the difference in the two potentials.

$$E_{\text{Cu}^{++}, \text{Cu}^+} = .167 + .059 \log \frac{[\text{Cu}^{++}]}{[\text{Cu}^+]}$$

$$E_{\text{Cu}^+, \text{Cu}^0} = .522 + .059 \log [\text{Cu}^+]$$

$$E_{\text{diff.}} = -.355 + .059 \log \frac{[\text{Cu}^{++}]}{[\text{Cu}^+]^2}$$

In the last equation $\frac{[\text{Cu}^{++}]}{[\text{Cu}^+]^2}$ is the equilibrium constant for the disproportionation $2 \text{Cu}^+ \rightleftharpoons \text{Cu}^{++} + \text{Cu}^0$. In this manner a value of K for the reaction was obtained which agreed quite well with the literature, and apparently supported their ingenious mechanism. Actually it now appears that the agreement was accidental and, since the difference between the potentials was only about 10 or 20 millivolts, the 355 millivolts difference in the E^0 values determined the magnitude of the constant. In fact, if the difference had been zero, much better checks for the value of K would have resulted.

Verdieck, Ksycki, and Yntema (30) studied the decomposition potentials of Co, Ni, and Cu in chloride and bromide solutions. They explain the shape of the current density--potential curve by assuming a different slow (rate determining) process at different points on the curve. Their contention was that at low current density, $\log I$ vs E being linear, the rate of discharge of cations is the slow step; at higher current density, I vs E being linear indicates that rate of growth of the crystal lattice is the determining factor; and

at still higher current density that the non-linearity of the curve showed that probably some concentration polarization enters in. These conclusions are based on the equations developed in 1931 by Erdey-Grúz and Volmer (8). If the slowest process is discharge of ions, the "overvoltage", η , is proportional to $\log I$. If crystal growth rate is the slowest, then $1/\eta \propto \log I$ for two dimensional growth rate or $1/\eta^2 \propto \log I$ for three dimensional formation of nuclei. If the rate at which the metal spreads from edges and corners is slow then $\eta \propto I$. These relations were justified mathematically and experimentally by determining that in the deposition of a metal, $\eta \propto I$ and with the aid of a microscope the crystals can be seen to grow from the edges and corners.

The older views of Le Blanc and Schick (20) that the dissociation of the complex ion is the slow step have been largely discarded today. Masing (25) in 1942 compared the two views and showed that data in the literature gave curves corresponding to the equations of Erdey-Grúz and Volmer (8).

The somewhat popular view that depositions made at varying current densities and having different crystal sizes would not show the same potential has been disproved by Adams and Brown (1) who determined the normal potential using various forms of copper as the standard state. The standard oxidation potentials (compared to the hydrogen electrode)

found by them have the following values:

Electrolytic copper	.3448	±	.0002
Crystals	.3472	±	"
Finely divided	.3452	±	"
Amalgam	.3502	±	"

These values are for the reaction $\text{Cu}^{++} + 2e \rightarrow \text{Cu}^0$, but it is not likely that the cuprous potential would have a larger variation, and therefore, a change of conditions during deposition should not change the potential more than a few tenths of a millivolt. The work of Adams and Brown supports an earlier statement made by Hunt (17) that the potential would not vary with the grain size provided only that the deposit is adherent and compact.

Probably the most accurate explanation for the adherent fine-grained deposits obtained from solutions containing complex ions is that of Levin (22). He maintains that the low and essentially constant concentration of the cations is responsible and verifies his suggestion by obtaining comparable results with solutions containing no complex ions and equivalent concentration in free cation. By rapidly moving the solution past the electrodes Levin obtained smooth bright deposits of copper from solutions ranging from 10^{-7} to 2.5×10^{-12} molar in copper sulfate. The only polarization he found was concentration polarization. In 1937 Levin and Essin (23) reported that the deposition of cuprous copper from

non-aqueous solutions involved only concentration polarization. This was an extension of the work of Essin and Alfimova (10) who had shown a year earlier that for zinc and copper in cyanide solutions the current density--potential curve could be explained by concentration polarization alone provided the amount of hydrogen liberated, the accumulation of cyanide ions near the electrode and the existence of two cuprocyanide complex ions were taken into account.

Náray-Szabó and Szabó (26) prepared solutions containing complex cuprous ions by electrolytically dissolving a copper anode in various halide solutions, in an atmosphere of hydrogen. They enclosed the cathode in a clay diaphragm to prevent deposition of the copper. At constant total chloride concentration it was found that Nernst's equation described the equilibrium potentials at higher total copper content than 0.04 molar, but at lower concentrations the slope was shown to be steeper than the theoretical 0.059. They suggested that the change of slope might be due to other complexes appearing (not likely at constant chloride ion concentration) or due to a change of the hydrogen ion activity by hydrolysis of the complex. This would affect the equilibrium reaction, $\text{Cu}^{++} + \frac{1}{2}\text{H}_2 \rightleftharpoons \text{Cu}^+ + \text{H}^+$, and would change the potential because of the constant pressure of hydrogen above the solution. In spite of this suggestion they continued their work in a hydrogen atmosphere and did not make any

determinations using other gases. The activity coefficient of the complex anion, CuCl_3^- , was determined by use of the Debye-Hückel limiting law, $-\log \gamma = A z_1^2 \sqrt{\mu}$. Náray-Szabó and Szabó (26) pointed out that since A is a constant dependant on the medium and conditions, the law could be applied to the concentrated constant composition chloride solutions that they used.

For the reaction, $\text{CuCl}_3^- \rightleftharpoons \text{Cu}^+ + 3\text{Cl}^-$, at constant chloride concentration, $\frac{[\text{Cu}^+]}{[\text{CuCl}_3^-]} = \text{Constant} = \frac{[\text{Cu}^+]}{c \cdot \gamma}$. Also, $[\text{Cu}^+]$ is proportional to c, the concentration of the complex, and therefore, γ , the activity coefficient of the anion, is a constant for a given chloride ion concentration. Since $-\log \gamma = C \sqrt{\mu}$, a plot of $-\log \gamma$ against the square root of μ will have a slope equal to the constant C. Experimentally this was found to be 0.234. Displacement of this line parallel with itself until the activity coefficient at infinite dilution equals 1 (that is, $-\log \gamma = 0$ when $\sqrt{\mu} = 0$) gives the activity coefficient of the complex anion for a given total ionic strength. The instability constant for the complex was reported by Náray-Szabó and Szabó to be 1.45×10^{-6} .

III. INVESTIGATION

A. Objectives

The calculation of the proper value at which to limit the cathode--solution potential in experimental depositions was the objective of this investigation. It was first necessary to verify that Nernst's equation described the equilibrium potentials in the chloride solutions used. The effect of varying both the chloride and copper concentrations had to be determined. After proving that the calculation of an equilibrium potential for given conditions was possible, the correction to be applied for concentration polarization and other effects, if present, was determined. The calculations were then shown to be compatible with empirical experimental results obtained by other investigators working with similar solutions.

B. Procedure

1. Apparatus

In any work with cuprous copper, rigid exclusion of oxygen is essential. Even momentary contact with air causes sufficient oxidation of cuprous ions to color the solution and consequent increase of copper concentration due to the reaction, $\text{Cu}^+ + \text{Cu}^0 \rightleftharpoons 2\text{Cu}^+$. In the present work nitrogen

was chosen for the inert atmosphere because of the ease of obtaining and purifying it. Nitrogen from a commercial cylinder was passed through a diffuser in alkaline pyrogallol (8 per cent pyrogalllic acid, 15 per cent potassium hydroxide) and then over metallic copper in a U-tube at 340°C . The copper removed traces of oxygen and also served as an indicator for the condition of the pyrogallol. The darkening of the copper occurred at a sharp boundary and when about a third of it had been oxidized the cupric oxide was reduced by passing hydrogen through the tube. The oxygen-free nitrogen was bubbled through a solution with the same acid and chloride concentration as that used in the determination before being introduced into the cell.

The reaction cell was a 300 ml. tall form lipless beaker closed with a rubber stopper (Fig. 1 a). Both the cell and the calomel reference electrode were placed in a thermostated water bath maintained at $25 \pm 0.1^{\circ}\text{C}$. The solution in the cell was stirred with a motor driven glass propellor and readings taken until the potential was constant. Usually 30 minutes to an hour was sufficient but in some cases (when copper dissolved) as long as six hours was required. For the determination of current density--potential data using platinum flags as electrodes a smaller cell was desirable and the author constructed the one shown in Fig. 1 b from a large test-tube. The capacity of this cell was about 75 ml.

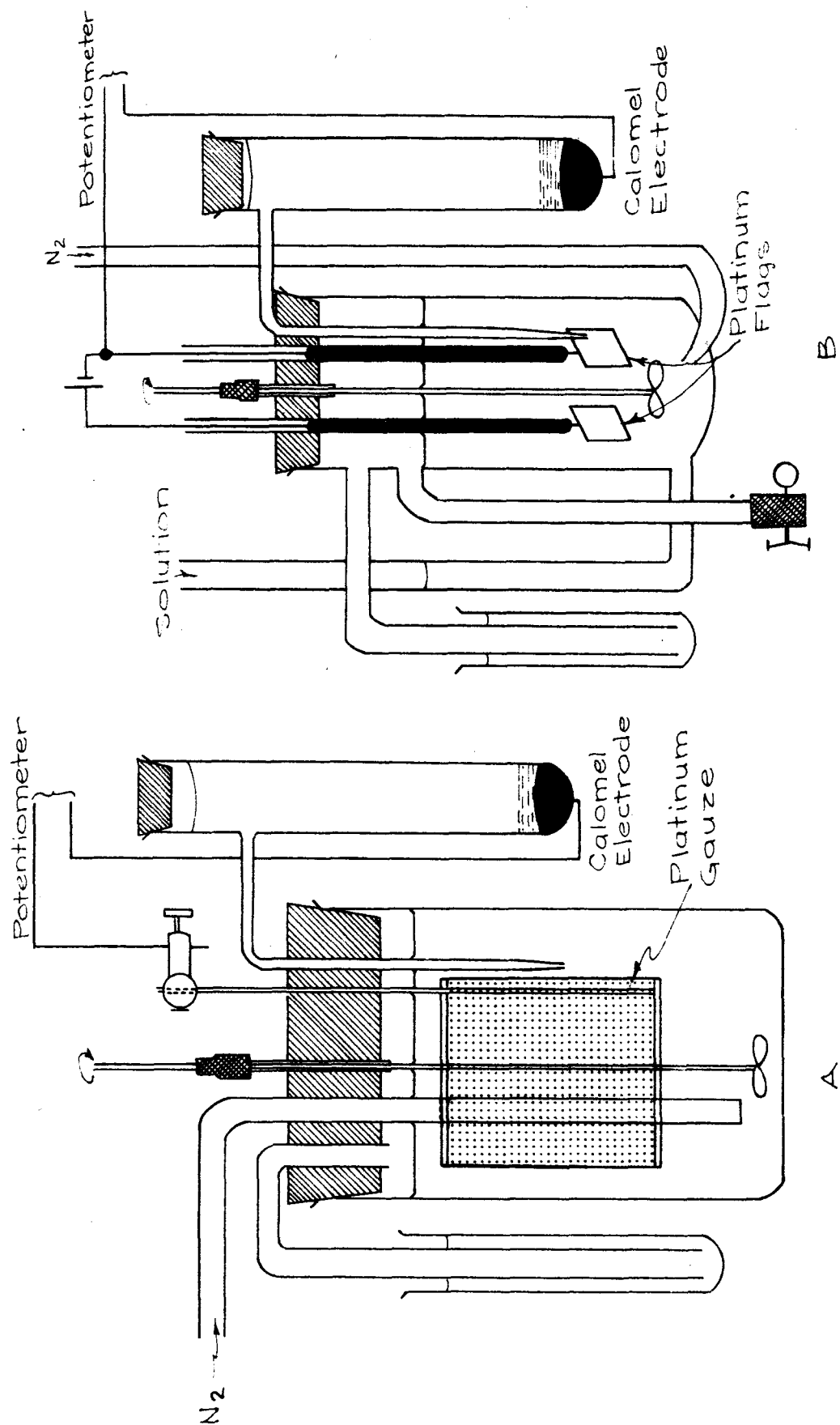


FIG. 1 CELLS USED FOR MEASURING COPPER POTENTIALS IN NITROGEN ATMOSPHERE

Potentials were measured against a saturated calomel reference electrode. Two home-made and two commercial type electrodes all checked to within 0.2 millivolts. Diffusion was minimized by using agar saturated with potassium chloride as the salt bridge. A Leeds and Northrup student type potentiometer was used to read the potentials. When it was learned that copper was dissolving in some of the solutions low in copper content, a Coleman Model 310 electrometer was substituted for the galvanometer in a number of determinations. According to the maker, this instrument has an input resistance of 10^{11} ohms. After establishing that current drawn in making the potential measurements was not the cause of the dissolution, the galvanometer was again used as a matter of convenience.

To determine concentrations of copper of the order of 10^{-6} grams per milliliter a sample of radioactive copper 64 was obtained from the Atomic Energy Commission. This isotope has a half-life of only 12.8 hours but has the advantage of producing no radioactive daughters. Cu^{64} emits electrons with 0.58 Mev energy to form Zn^{64} and emits positrons with 0.66 Mev energy to form Ni^{64} . By the time the sample had arrived, eight hour tolerance for gamma radiation was 4 inches so no elaborate precautionary measures were necessary in handling the sample. Counting the samples was accomplished by using a Geiger-Mueller tube and an Instrument Development

Laboratories Model 165 Sealing Unit.

The electron diffraction patterns were made with an RCA electron microscope. The copper deposits were made on platinum flags 0.5 by 1 cm. and held in a slot on a tiny brass tube attached to the specimen holder. The copper plated flags were rinsed with water and acetone then allowed to dry at room temperature, only a minute or two being required, before introducing into the instrument. A collodion transparency from a silver deposit was used for comparison of crystal structure and spacing.

Current density--polarization curves were made for both the platinum gauze cathodes and platinum flags (about 4 cm² total area). To aid in maintaining constant concentration of the solutions, electrolytic copper was used as the anode. Potentials were measured with a saturated calomel electrode and potentiometer. Current was drawn from a lead storage cell and was measured with Weston 0-5 and 0-300 milliammeters. After completing a series of determinations several values of current were rechecked to assure reproducible values.

2. Preparation and Analysis of Solutions

Cuprous chloride can be kept pure only when sealed and stored in the dark. The freshly opened reagent grade cuprous chloride was always quite green and contained considerable divalent copper. In the present work solutions were made to

approximate concentrations and analyzed after the potential measurements. Solid cuprous chloride was dissolved in dilute hydrochloric acid, diluted to volume, and stored with metallic copper ribbons for a day or two until colorless. Samples were withdrawn by pipet and introduced directly into the nitrogen filled cell through the hole in the stopper for the calomel electrode. All solutions were colorless when used. The copper reference electrode was prepared by electrodeposition on platinum gauze from a hydrochloric acid solution containing 16 grams hydroxylamine hydrochloride per liter as anodic depolarizer.

Equilibrium potentials were determined in 0.5 to 2.25 molar chloride solutions with the total copper content varying from 0.002 to 0.265 molar. Total copper was determined by taking 50 or 100 ml. samples, adjusting the total chloride concentration to 1.75 with hydrochloric acid, and adding hydroxylamine hydrochloride. This is according to the procedure of Diehl and Brouns (7) except that as copper was the only heavy metal present, the cathode potential did not need to be limited. The chloride was determined volumetrically with 0.1 N silver nitrate using dichlorofluorescein as adsorption indicator. The silver nitrate was standardized by weight and by the same volumetric method using reagent grade potassium chloride. The procedure for this determination is described in elementary textbooks on quantitative analysis

(see Willard and Furman (31)). Samples were taken with a 5 ml. pipet or with a 5 ml. buret and were in all cases at least 2 ml. This method gave an accuracy well within the one per cent considered sufficient because of the assumptions used in calculating the activity coefficients. Preliminary oxidation to break down the complex, CuCl_3^- , was necessary to get a good endpoint in the titration for chloride. This oxidation was carried out in various ways; air, oxygen, nitric acid, and hydrogen peroxide all being tried. The best results were obtained by adding 2 ml. of three per cent hydrogen peroxide after neutralizing the acid with excess calcium carbonate (chloride free). This treatment also oxidized the hydroxylamine hydrochloride present in some of the solutions. To determine acid a titration with 0.1 N sodium hydroxide to the methyl orange endpoint was used. After adding the hydrogen peroxide, chloride was determined on the same sample. In one series of determinations the total copper concentration varied from 5×10^{-4} molar to 1.6×10^{-3} molar and was determined colorimetrically using a Coleman Model 11 spectrophotometer. The procedure was that of Center and MacIntosh (6) using rubeanic acid. To eliminate free mineral acid the 50 or 100 ml. sample was evaporated with 2 ml. of concentrated sulfuric acid and fumed to dryness. The salts were dissolved in hot distilled water and diluted in a volumetric flask from which samples containing about .2 milli-

grams were pipetted.

A sample of radioactive copper wire (Cu^{64}) weighing 0.1120 grams was dissolved in 25 milliliters of dilute (1 to 1) HCl by adding 2 ml. 30 per cent hydrogen peroxide and diluted to 100 ml. One milliliter of this solution diluted to 100 ml. was kept for a standard and had a concentration of 11.2 micrograms per milliliter. A copper deposit was prepared on a platinum flag by electrolysis of 50 ml. of the solution with one gram of hydroxylamine hydrochloride added. Using 25 milliamperes total current a bright adherent deposit was obtained in thirty minutes. Solutions were analyzed by withdrawing 1 milliliter samples in an ordinary pipet with a rubber syringe attached. The syringe was then slipped off and the draining controlled in the usual manner by hand. The samples were evaporated to dryness on 2 inch watch glasses on an electric hot plate, and concentrations determined by counting with a Geiger-Mueller tube.

Determination of counts for standards were made in the same manner and repeated every two or three hours. A plot of log counts per minute vs time for 1 ml. of standard gave a straight line and was used to determine the counts per minute per microgram at the time each sample was counted. All counts were corrected by adding one per cent per 1000 counts per minute for coincidence counting and by subtracting 52 counts

per minute for background. The background was determined continuously whenever the counter was not being used for samples or standards.

C. Experimental Results

Equilibrium potentials were determined in a series of solutions with constant chloride concentration and varying amounts of cuprous copper. A plot of log total copper against potential gave the family of parallel lines shown in Fig. 2. The lines are drawn with a slope of 0.059 in accordance with Nernst's equation for a reaction involving one electron. The data from which the points were plotted is recorded in Table 1. When one notes that the chloride concentrations varied somewhat and that an increase in chloride gives a more negative potential, these points lie quite close to the theoretical slope predicted by Nernst's equation. At a single total copper concentration (0.02 molar) the potential was plotted against log of the chloride ion activity. This curve is shown in Fig. 3 and the data from which the curve was plotted is recorded in Table 2. The line has a slope of $.059 \times -3.01$.

The activity coefficient of a single ion cannot be determined but a reasonable and widely accepted assumption is that the activity coefficient of the two ions are equal in

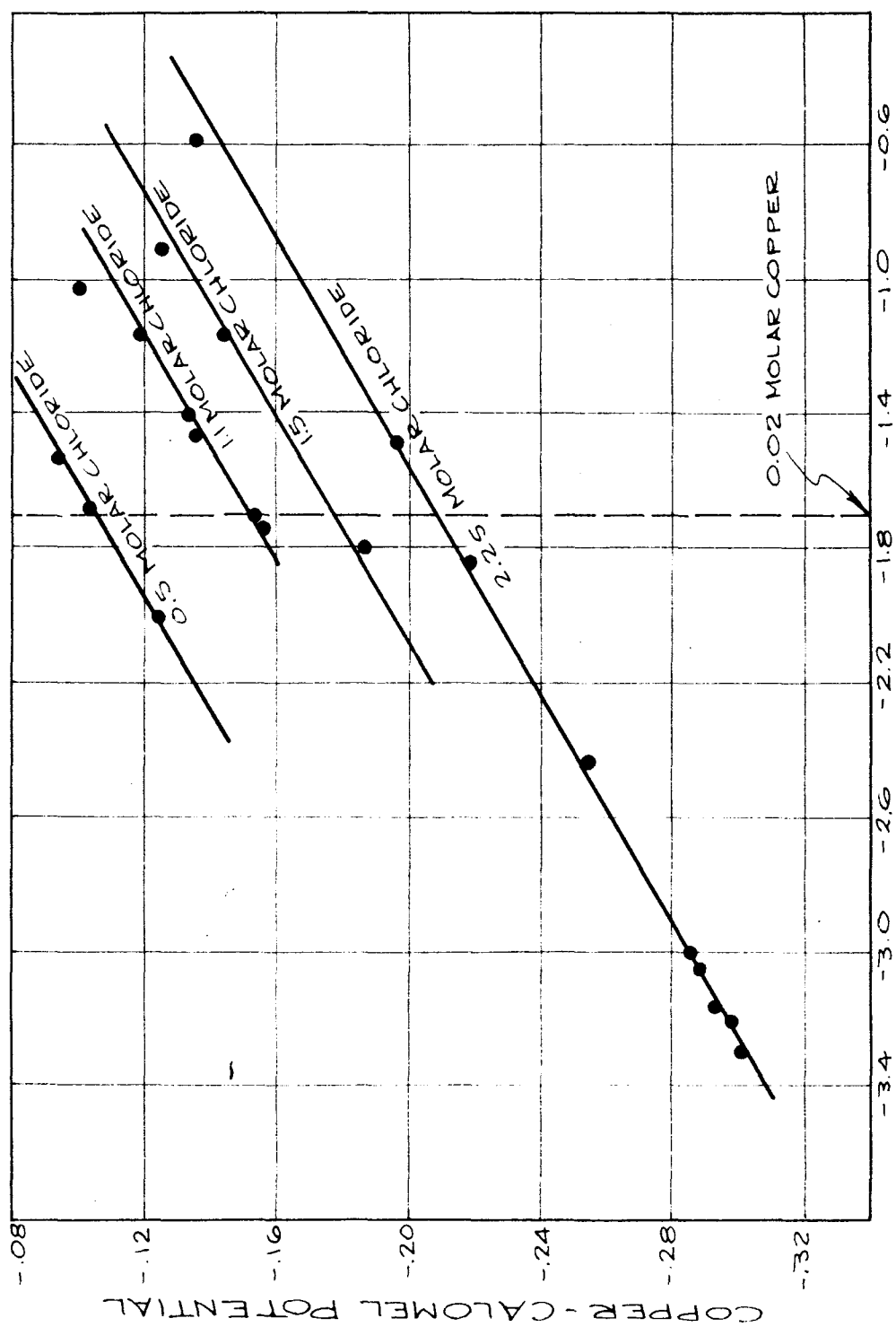


FIG. 2 EQUILIBRIUM POTENTIALS IN CHLOROCUPROUS SOLUTIONS

TABLE 1
Equilibrium Copper Potentials in Various
Chlorocuprous Solutions^a

Potential (vs. sat. calomel)	Total chloride conc. moles/liter	Total copper conc. moles/liter
-0.0940	0.500	0.0294
-0.1027	0.506	0.0210
-0.1243	0.514	0.0100
-0.1103	1.18	0.0924
-0.1339	1.14	0.0397
-0.1527	1.12	0.0194
-0.1252	1.55	0.127
-0.1442	1.52	0.0695
-0.1873	1.49	0.0163
-0.1351	2.37	0.265
-0.1963	2.28	0.0363
-0.2186	2.25	0.0147
-0.2542	2.24	0.00368
-0.2850	2.26	0.00097
-0.2880	2.25	0.00089
-0.2930	2.26	0.00067
-0.2980	2.25	0.00061
-0.3020	2.25	0.0005
-0.1183	1.10	0.0686
-0.1325	1.04	0.0375
-0.1523	1.02	0.0184

^aThe last three solutions were equimolar sodium chloride and hydrochloric acid. All the others were hydrochloric acid.

TABLE 2
Equilibrium Copper Potentials in Solutions of
Varying Chloride Activity and Constant Total Copper

Potential (vs. sat. calomel)	Total chloride moles/l.	γ_{Cl^-}	$[Cl^-]$
-0.105	0.50	0.651	0.326
-0.150	1.05	0.599	0.629
-0.152	1.15	0.596	0.687
-0.181	1.50	0.578	0.878
-0.211	2.25	0.573	1.29

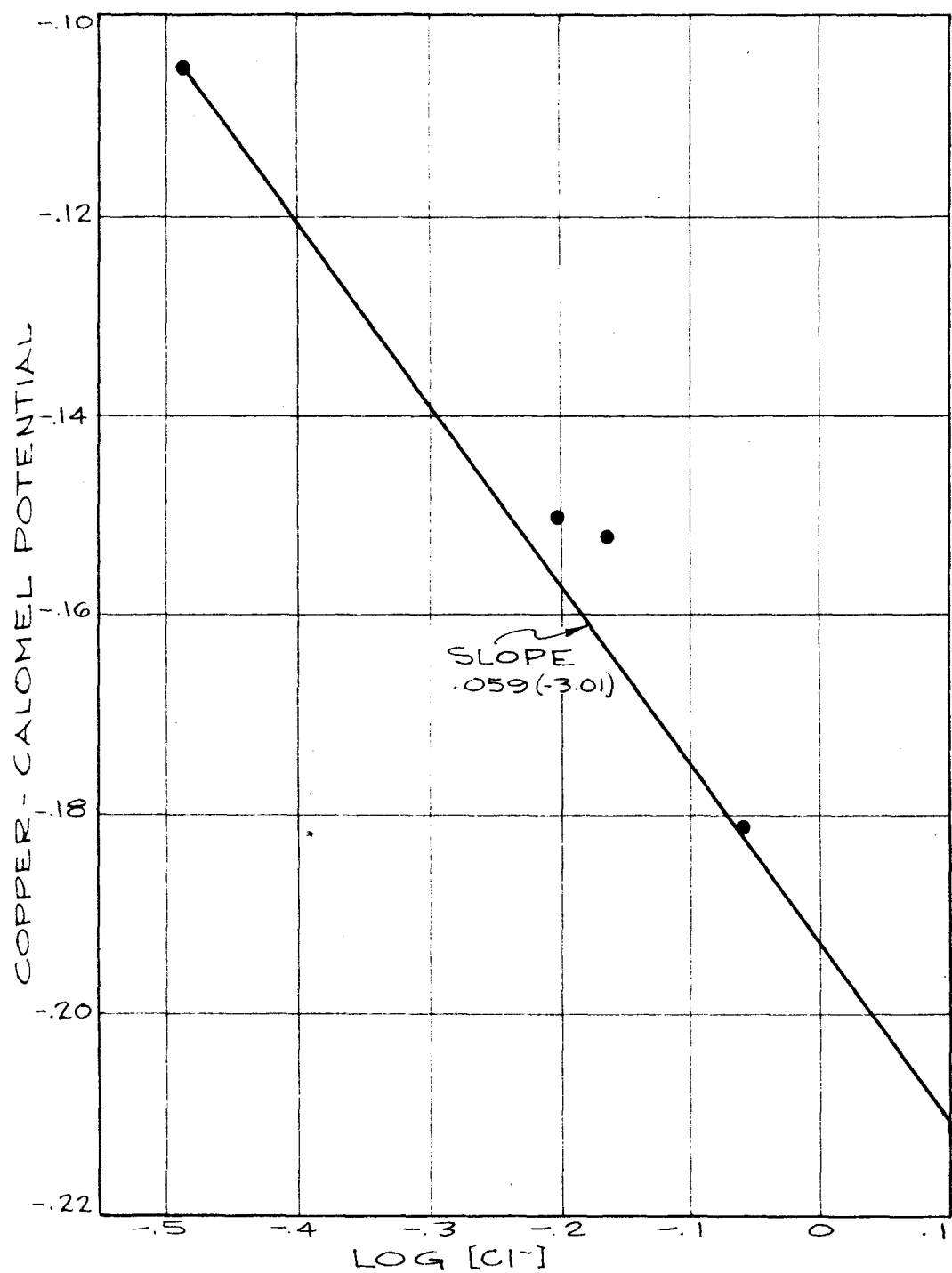


FIG. 3 EQUILIBRIUM POTENTIALS IN CHLORIDE SOLUTIONS CONTAINING 0.02 MOLES PER LITER TOTAL COPPER

solutions of potassium chloride and therefore that the activity coefficient of the chloride ion in a solution is equal to the mean value for potassium at the same total ionic strength. The values used in Table 2 were obtained by graphical interpolation of the values of gamma for potassium chloride reported by Harned and Cook (15).

When the copper concentration of the solution was reduced to too low a value copper dissolved in the chloride solution. A series of determinations of the time--potential curves for copper in contact with chloride solutions showed that the potential rapidly dropped to a minimum after about 12 minutes and then rose about 5 millivolts to a constant value. A typical curve is marked a and reproduced in Fig 4. If the copper was etched with dilute nitric acid and then washed with distilled water, a time--potential curve of the type marked b in Fig. 4 resulted. If the copper which had been etched was used successively in a series of pure chloride solutions the time--potential curve gradually changed and approached the shape of curve a. The constant potentials in this work were not reproducible but varied over a rather wide range for the same chloride concentration. Table 3 shows a few of the constant potentials obtained with molar chloride solutions.

The equilibrium potential did not correspond with the total copper content of the final solution but the amount that

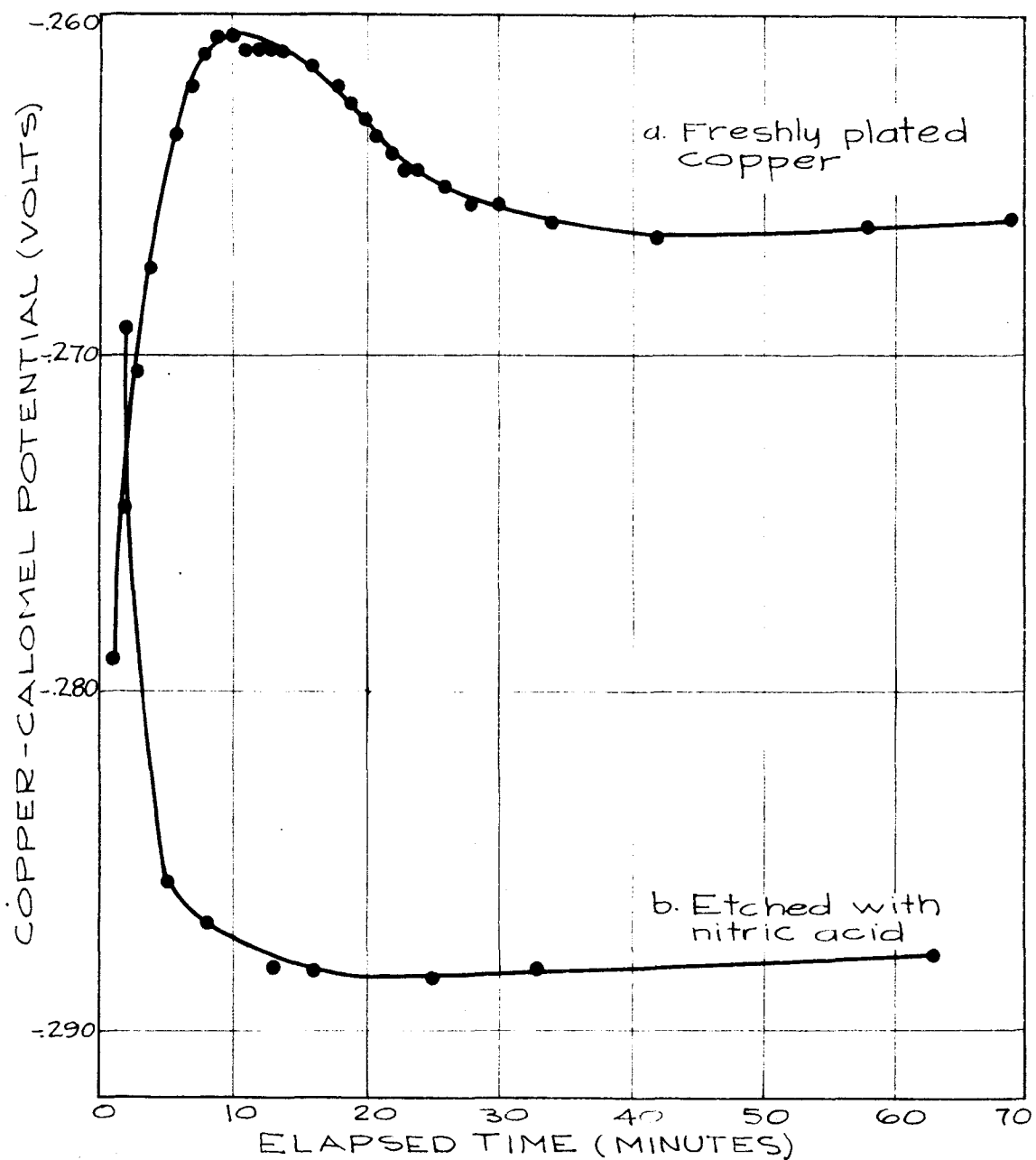


FIG. 4 CHANGE OF POTENTIAL WITH TIME FOR COPPER IN PURE CHLORIDE SOLUTION

dissolved depended on some uncontrolled variable. The nature of the surface of the copper was that variable.

TABLE 3

Equilibrium Copper Potentials
in Molar Chloride Solutions

Solution	Equilibrium Potential
1 M HCl	-0.2640
"	-0.2800
0.5 M HCl, .5 M KCl	-0.2615
"	-0.2915
1M KCl	-0.2880

Radioactive copper was used to gain further knowledge of the course of the time--potential curve. The copper was electrodeposited on a platinum flag and brought into contact with approximately 1.7 molar hydrochloric acid in a nitrogen atmosphere. Potentials were measured against a saturated calomel electrode and 1 milliliter samples withdrawn for determination of copper concentrations. The data obtained is recorded in Table 4 and Figure 5 shows the results graphically. These results established that the potential does not follow the copper concentration at very low concentrations. The time required to reach equilibrium was longer due to the small area of the platinum flag as compared to the platinum gauze used in earlier determinations. This slowing of the rate was desirable because of the manipulative difficulties in following both curves simultaneously in the early part of

TABLE 4

Change of Potential and Copper Concentration
with Time in 1.7 Molar Hydrochloric Acid

Elapsed time (minutes)	Potential (vs. sat. cal.)	Copper Concentration (milligrams per liter)
1	-0.4375	
2	-0.4275	1.80
3	-0.4255	
4	-0.4248	1.95
5	-0.4250	
6	-0.4250	2.08
7	-0.4250	
8	-0.4255	2.02
9	-0.4261	
10	-0.4261	2.12
12	-0.4262	2.11
14	-0.4263	2.27
18	-0.4260	2.38
22		2.48
30	-0.4268	2.97
41	-0.4282	
73	-0.4300	3.50
140	-0.4333	4.77
275	-0.4362	
280		7.0
350	-0.4368	
420	-0.4377	8.4
1115	-0.4457	11.4
1185	-0.4498	10.8
1275	-0.4498	12.4
1305	-0.4498	13.0

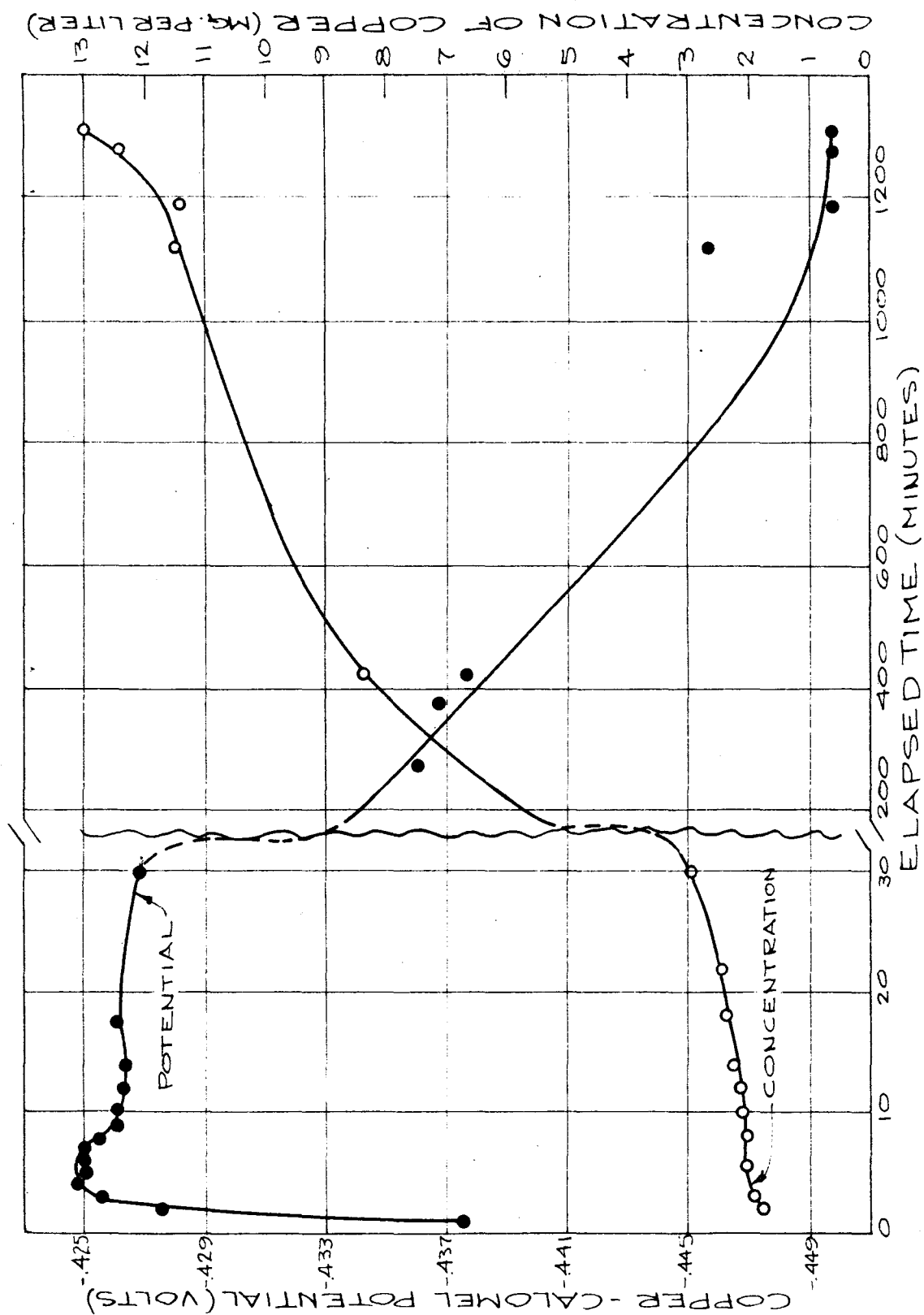


FIG. 5 POTENTIAL AND COPPER CONCENTRATION IN 1.7 MOLAR HYDROCHLORIC ACID

the experiment.

To determine whether or not there is exchange between metallic copper and solutions containing chlorocuprous ions, the copper plated flag was brought in contact with approximately 1.7 molar hydrochloric acid containing cuprous copper. The potential measurements established that the copper was at equilibrium with the solution and the rapid increase in active copper in the solution proved an exchange. The decay of the radioactive copper prevented continuing the measurements to equilibrium, but the data presented in Table 5 shows the rapid increase in the concentration of radioactive copper in solution.

TABLE 5

Exchange between Metallic Radioactive Copper
and 1.7 Molar Hydrochloric Acid Solution
containing Cuprous Chloride

Elapsed Time (minutes)	Potential (vs. sat. cal.)	Radioactive Copper Concentration (milligrams per liter)
1	-0.4332	
5	-0.4418	
11	-0.4420	2.2
34	-0.4426	
46	-0.4427	
76	-0.4418	5.0
136	-0.4428	7.8
286	-0.4450	13.3
376	-0.4456	17.0

To study the nature of the copper surface an examination of various deposits was made by electron diffraction. Specimens were plated on a platinum flag 0.5 by 1 cm. Examination was made of the platinum flag and of several copper deposits. A very thin deposit only partially covering the platinum, a bright adherent deposit, and a red spongy deposit resulting from simultaneous deposition of hydrogen all showed the same crystal structure. As expected etching of the copper with nitric acid did not change the electron diffraction pattern. The platinum surface was amorphous. This explains the abnormally high potential required to start the formation of copper nuclei--the so-called supersaturation in electrodeposition studied by Erdey-Grúz and Volmer (9). After etching with aqua regia the diffraction pattern of the platinum showed crystal structure similar to copper but with a preferred orientation. The plates are reproduced in Fig. 6.

To determine the magnitude of the polarization a series of current density--polarization curves were plotted. Since there was some doubt as to the true surface area of a crystalline deposit, the total current and approximate area of the cathodes, were recorded. Fig. 7 compares at approximately equal current density the curves obtained with a gauze cathode (150 cm^2) and a platinum flag (4 cm^2). The data from which these curves were plotted is shown in Table 6.

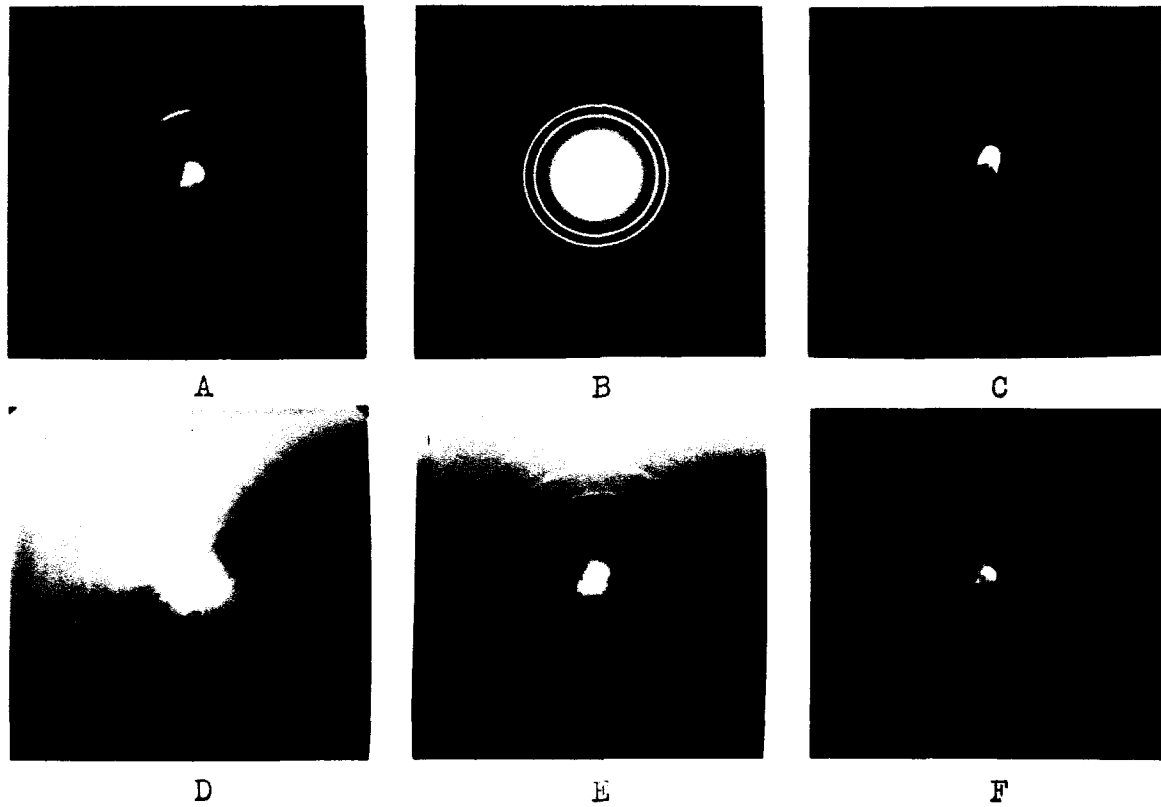


Fig. 6 Electron Diffraction Patterns

- A. Platinum surface after etching with aqua regia.
- B. Silver transparency for comparison of structure.
- C. Thin copper deposit made at low current density.
- D. Normal bright copper deposit.
- E. Red spongy copper deposit made at high current density.
- F. Copper deposit after etching with nitric acid.

TABLE 6

Cathode Potentials during Electrolysis in 1.75 Molar
Hydrochloric Acid with Constant Copper Concentration

Platinum Gauze		Platinum Flag	
Potential (sat. cal.)	Total current (mamps.)	Potential (sat. cal.)	Total current (mamps.)
-0.1395	20	-0.1343	0.5
-0.1377	40	-0.1362	1.0
-0.1390	40	-0.1376	1.5
-0.1410	50	-0.1398	1.8
-0.1428	50	-0.1406	1.9
-0.1413	60	-0.1418	2.0
-0.1472	70	-0.1506	2.2
-0.1488	70	-0.1530	2.4
-0.1510	80	-0.1536	2.5
-0.1565	85	-0.1550	3.0
-0.1600	90	-0.1575	3.5
-0.1640	100	-0.1585	4.0
-0.1656	120	-0.1588	4.4
-0.1700	150		
-0.1725	175		
-0.1750	200		

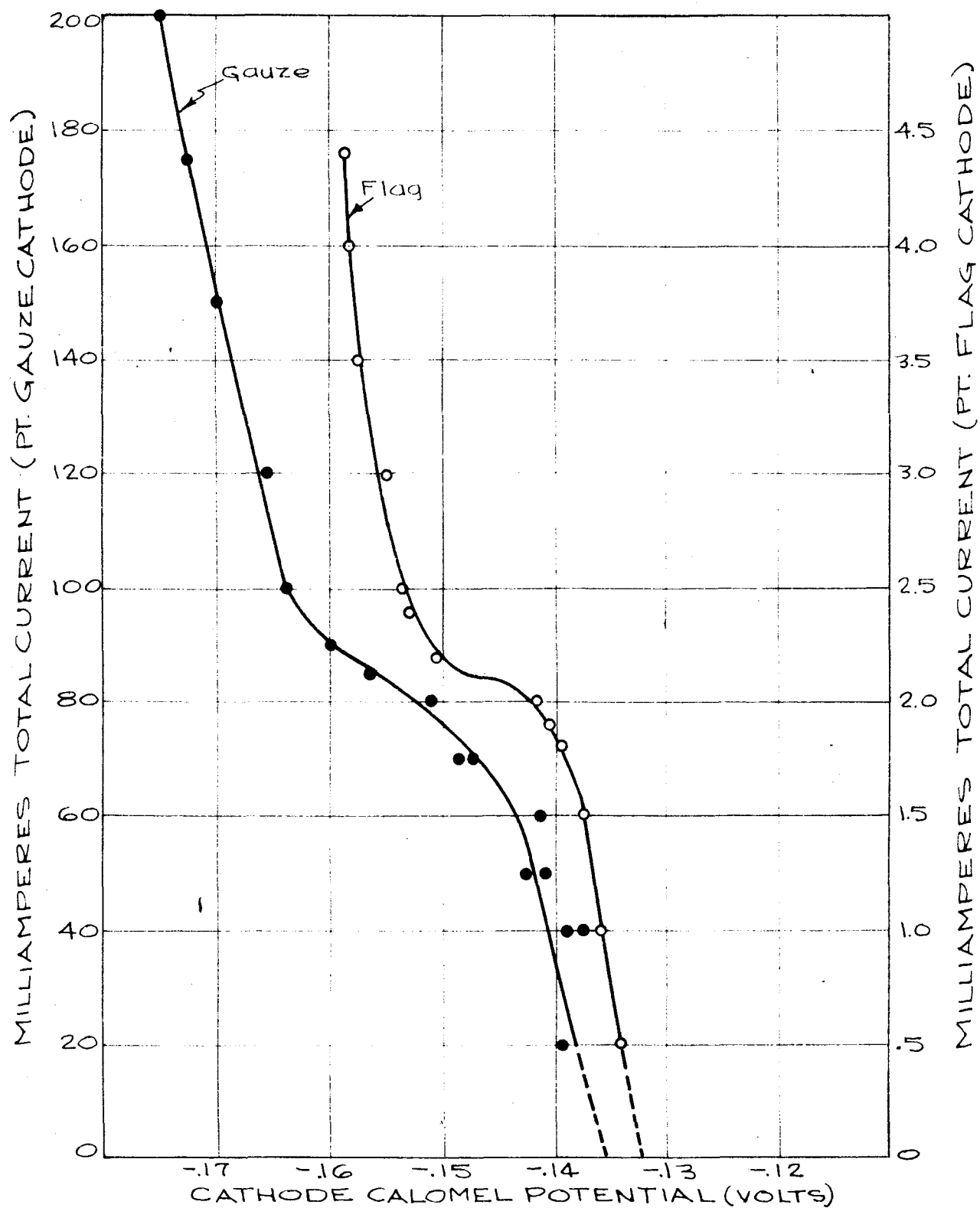


FIG. 7 ELECTROLYSIS WITH COPPER ANODE IN 1.75 M HCL

As expected, the gauze showed more polarization than the flag since stirring was more difficult. The solution used for the flag was purposely made slightly higher in copper content so that the curves would not overlap.

From a practical standpoint it was important to determine how exact the concentrations must be controlled in an actual deposition to maintain reasonable accuracy. This was especially important since common practice has always been to wash down the sides of the cell with water near the end of the electrolysis without paying any particular attention to the final volume. The copper--solution potential depends on the activity of free cuprous ion in solution and this in turn is dependent on the chloride ion activity because of the complex formation. The instability constant for the ion, CuCl_3^- , was calculated by Diehl and Brouns (7) from solubility data in the literature as 1.23×10^{-6} . Náray-Szabó and Szabó (26) found 1.45×10^{-6} from potential measurements. The latter value will be used for calculations. For the electrode reaction, $\text{Cu}^+ + e \rightarrow \text{Cu}^0$, the potential is described by $E = E^0 + .059 \log [\text{Cu}^+]$ ($E^0 = .522$) and the cuprous ion activity may be calculated from the expression, $K = \frac{[\text{Cu}^+][\text{Cl}^-]^3}{[\text{CuCl}_3^-]}$. The activity coefficient of the complex was found from the Debye-Hückel limiting law, $-\log \gamma = 0.234 \sqrt{\mu}$. The constant, 0.234, was determined experimentally for similar solutions by Szabó. Mu

is the ionic strength of the solution. In the procedure of Diehl and Brouns the electrolytic solution had the following approximate composition:

Constituent	Moles Chloride	Chloride Concentration (based on 250 ml.)
0.5 - 1 gram sample		
30 milliliters concentrated hydrochloric acid	0.3645	1.458
4 grams hydroxylamine hydrochloride	0.0575	0.230
0.4 grams tin as stan- nous chloride	0.0108	<u>0.0432</u>
Total		1.731

The concentrations of the ions present at the end of the electrolysis are: Chloride, 1.73; stannic, 0.025; and hydrogen, 1.63 (by difference). These values were calculated on the reasonable assumption that all tin had been oxidized to the quadrivalent state either by cupric or by air at the end of the electrolysis. On the basis of these values,

$\mu = \frac{16 \times 0.025 + 1.63 + 1.73}{2} = 1.88$ and $-\log \gamma = .234 \times \sqrt{1.88}$. This gave a value of 0.478 for the activity coefficient of the chlorocuprous ion. If the concentration of the stannic ion is doubled, gamma is 0.460--showing the negligible effect of the other constituents in the sample than copper. Changing the chloride ion concentration by adding three milliliters less hydrochloric acid (0.036 moles), an error of ten per cent, gave a gamma value of 0.482. Finally,

if the final volume was 275 instead of 250 milliliters, gamma had a value of 0.495. Thus, the activity coefficient of the complex was changed by less than two per cent by any of these errors. When this change was substituted in the calculations for E it had a negligible effect on the limiting potential (less than 1 millivolt).

The effect of concentration errors on the chloride ion activity, which appears in the expression for K as the third power, was then calculated. An error of ten per cent (three milliliters less) in measuring the hydrochloric acid added caused the potential to be 1.1 millivolts less. If the final volume was 275 milliliters, the chloride concentration was 1.57 instead of 1.73, and the potential was decreased by 7.1 millivolts. These considerations showed that no great accuracy in measuring the hydrochloric acid added and only reasonable care in limiting the final volume were necessary for maintaining accuracy.

Several attempts to get an electrodeposit of copper on glass fibers attached to the cathode gave negative results. It was reported in 1939 (14) that copper had been deposited on glass from cyanide solutions. The evidence submitted was "before and after" photographs. In the present investigation a single glass fiber was held against a platinum flag by a drop of lable varnish at each end. After plating copper on the flag from a chloride solution, a second fiber was

attached near the first and the flag examined with a microscope (50X magnification). No copper could be detected on the fibers but it was noted that if the focal plane was slightly raised, both fibers appeared to be covered with copper. The earlier investigators in taking separate photographs before and after a deposition may have been misled by this illusion. Their experiment with cyanide solutions was not repeated.

IV. DISCUSSION

A. Electrode Reaction

In chloride solutions of cuprous copper most of the copper exists as the chlorocuprous complex, CuCl_3^- , but free cuprous ions are in equilibrium with this complex, the instability constant being about 10^{-6} . For a particular chloride ion activity (and temperature), the ratio of cuprous to chlorocuprous ions is constant, and Nernst's equation holds whether cuprous, chlorocuprous, or total copper activities are used. Furthermore, the calculated potential for given copper content will agree with one determined experimentally provided the correct corresponding E° value is used. The number of electrons involved determines the slope but it has not been possible to determine the actual electrode reaction. E° for the reduction of cuprous to metallic copper is 0.522 toward the normal hydrogen electrode. Diehl and Brouns (7) calculated that the E° for the reaction,



would be 0.178. Since the value of K was involved in their calculations of E° , it is evident that computation of the E value for given amount of copper by either $E = E^\circ + .059 \log [\text{Cu}^+]$ or $E = E^\circ + .059 \log \frac{[\text{CuCl}_3^-]}{[\text{Cl}^-]^3}$ will give the same potential. It seems more likely that the free ions are reduced than that a doubly negative charged anion should be reduced at the cath-

ode. It is true that the concentration of free ions is extremely low, but Levin (22) demonstrated that electrolysis is possible in concentrations as low as 2.5×10^{-12} moles per liter, and that is much less than the copper concentration at the end of the electrolysis. In the present investigation the log of the total copper (essentially equal to CuCl_2) in solution was plotted against the potential at constant chloride concentration, and the log of the chloride ion activity was plotted against the potential at constant copper concentration. This method avoided the question as to the actual electrode reaction but calculations involving changes of both copper and chloride concentrations may be made equally well with either electrode reaction and in either case the activity coefficients for both the chloride and chlorocuprous ions must be used.

B. Cathode Polarization

It is only near the end of an electrolysis that polarization is apt to be important in electrodeposition with controlled cathode potential. The limiting potential is determined for the residual concentration of the element being determined. At early stages in the electrolysis the concentration of the metal ion is so much greater that a large polarization would not bring the potential above the limiting potential. At the end of an electrolysis the total

current (gauze electrode) has been reduced to 20 or 30 milliamperes and the polarization (see Fig. 6) is less than 10 millivolts.

The flat portion of the current density polarization curve is due to a change of electrode reaction. The lower branch shows polarization involved in the deposition of copper alone and the upper branch involves simultaneous discharge of copper and hydrogen. This suggestion was made by Essin and Matanzew (11) for cyanide solutions and substantiated the work of Glasstone (13) who had determined the current efficiency in solutions containing complex cuprous ions. As the cuprous ions are depleted in the cathode boundary layer by deposition their activity is reduced until hydrogen is also discharged. Hydrogen ions are replaced by diffusion faster than cuprous so progressively a greater proportion of hydrogen is discharged until a vigorous evolution of the gas makes the copper deposit spongy.

C. Indicator Electrode

The present investigation established experimentally that copper dissolved quite rapidly in chloride solutions containing low concentrations (less than about 10^{-4} moles/l.) of copper. This suggested that an indicator electrode of copper would not trace the equilibrium potential of the solution to the end of the deposition because the copper dissolving must

diffuse out of the electrode boundary layer and, therefore, also would show concentration polarization. This polarization was established by the potential--time measurements with chloride solutions low in copper. As the copper dissolved the chloride ion activity in the boundary layer was decreased due to complexing and an abnormally low potential resulted. In a few minutes, after the chloride was uniformly distributed throughout the solution, the potential reached a higher and equilibrium value. This suggestion qualitatively explained the "hump" in the curve shown in Fig. 4 a and in Fig. 5. Similar "humps" were obtained by Gauvin and Winkler (12) while making potential measurements in copper sulfate solutions but they offered no explanation for the cause.

An explanation for curve b in Fig. 4 is more difficult to devise but it is probable that after treatment with nitric acid the copper was covered with an oxide layer which changed the standard reference potential. As the coating dissolved the potential rose to the true equilibrium value.

D. Calculation of Limiting Potential

In a solution which has a chloride ion activity of one, (1.73 molar) the potential for 0.02 molar total copper is -0.191 volts toward a saturated calomel electrode. This value was obtained from Fig. 3. Applying the slope 0.059 according to Nernst's equation,

$$0.059 = \frac{-0.191 - E(\text{limit})}{\log .02 - \log 10^{-6}}$$

The limiting potential for a solution with 10^{-6} moles per liter residual total copper is calculated to be -0.445 volts relative to saturated calomel. Brouns (3) used solutions of approximately 0.6 molar chloride concentration and deposited copper quantitatively at a limiting potential of -0.40 volts. For 0.6 molar chloride the potential calculated as above is -0.371 and allowing for concentration polarization any potential more negative than -0.380 should allow for complete deposition of the copper.

The correct limiting potential for a particular chloride ion activity may be calculated by determining from the graph in Fig. 3 the equilibrium potential for a solution 0.02 molar in copper and subtracting 0.254 [that is, $0.059 (-1.7 + 6)$] from it. This gives the equilibrium potential for a solution 10^{-6} molar in total copper, and an addition 10 millivolts will allow for concentration polarization. If a hydrochloric acid solution of the same molarity is used to rinse the sides of the beaker, the final volume of electrolyte will have little effect.

E. Activity Coefficient of the Complex

In strong chloride solution practically all of the copper exists as an ion, $\text{CuCl}_x^{(x-1)-}$ and for the hypothetical reaction,

$\text{CuCl}_x^{(x-1)-} + e \rightleftharpoons \text{Cu}^0 + x \text{Cl}^-$, the potential is defined by
 $E = E^0 + .059 \log \frac{[\text{CuCl}_x^{(x-1)-}]}{[\text{Cl}^-]^x}$. For constant concentration

$$\begin{aligned} \text{of the complex, } E &= E^0 + 0.059 \log [\text{Cl}^-]^{-x} + C \\ &= E^0 - 0.059 x \log [\text{Cl}^-] + C. \end{aligned}$$

From this equation it is evident that if a plot of E against $\log [\text{Cl}^-]$ is made the slope will be $-0.059 x$. Fig 3 shows this plot for 0.02 molar total copper. The slope is $-0.059 \cdot 3.01$ and shows in a new way that the chlorocuprous complex contains three chloride ions in the range between 0.5 and 2.25 molar chloride. E^0 for this reaction was calculated by Diehl and Brouns (7) as 0.178 or -0.068 against saturated calomel. The above equations show that at the intercept in Fig. 3 (that is, when the activity of the chloride ion equals one) the measured potential is the sum of E^0 and $0.059 \log [\text{CuCl}_3^-]$. In this way the activity of the chlorocuprous ion may be calculated and since the concentration is 0.02 the activity coefficient of the complex can be determined. The potential of the intercept is -0.191 and, therefore,

$$\log [\text{CuCl}_3^-] = \frac{.068 - .191}{.059} = -2.085.$$

$[\text{CuCl}_3^-] = 8.22 \times 10^{-3}$ and the activity coefficient of the chlorocuprous ion is 0.41. This value is in reasonable agreement with the 0.48 calculated from the Debye-Hückel limiting law for the same total chloride concentration. The constant in the Debye-Hückel equation was that obtained by Náray-Szabó

and Szabó (26), 0.234.

V. CONCLUSIONS

1. The equilibrium potential for copper in 0.5 to 2.25 molar chloride solutions followed Nernst's equation to 5×10^{-4} molar total copper.

2. By plotting equilibrium potentials against log of the chloride ion activity at constant copper content the formula for the chlorocuprous ion was shown to be CuCl_3^- . The activity coefficient of the complex ion was calculated from this curve.

3. Metallic copper in contact with very dilute cuprous solutions (0.5 to 2.25 molar in chloride) did not measure the reversible potential because it rapidly dissolved. Measurement of copper concentrations with radioactive copper proved that the potential did not indicate the copper concentration.

4. Concentration polarization in chlorocuprous solutions was less than 10 millivolts at the end of electrolysis and thus had negligible effect on the limiting potential for controlled cathode potential work.

5. Over a wide range of current densities a copper deposit had the same crystalline nature as shown by electron diffraction patterns.

6. The limiting potential for depositing copper from chloride solutions was calculated. Reasonable variations

of concentration in carrying out a deposition did not appreciably change this potential.

7. There is an exchange between metallic copper and chloride solutions of cuprous copper.

VI. SUMMARY

Working in a nitrogen atmosphere the potentials between metallic copper and various cuprous chloride solutions were determined and were shown to follow Nernst's equation at least down to 5×10^{-4} molar total copper. Chloride solutions from 0.5 to 2.25 molar were used. In this range of chloride concentrations the formula for the chlorocuprous complex ion was proved to be CuCl_3^- by a new method, and the activity coefficient for the ion was calculated for a solution 1.73 molar in chloride and 0.02 molar in total copper.

In very dilute cuprous solutions metallic copper rapidly dissolved. Both the shape of the time--potential curve and the final equilibrium potential depended on the prior treatment of the copper to a considerably greater extent than on the chloride concentration. By tracing the copper concentration with radioactive copper it was shown that the potential did not depend on the copper concentration in very dilute solutions. The common practice of using a copper wire to indicate the equilibrium potential and thus the activity of the metal ions in solution did not give the correct results when the solution contained very small amounts of copper, due to this dissolution of copper. An exchange between metallic copper and cuprous copper in chloride solutions was established using radioactive copper.

By plotting current--potential curves and extrapolating to zero current, concentration polarization was shown to be less than 10 millivolts for the solutions used at current densities of less than 0.3 milliamperes per square centimeter. Since lower current densities than this are used at the end of electrolysis with controlled cathode potential, the concentration polarization was shown to have little effect on the limiting potential. The plateau shown by the current--potential curves was explained as being due to simultaneous deposition of hydrogen and copper. Deposits made at higher and lower current densities than this plateau showed no difference in crystal structure when examined with a microscope and an electron microscope.

To calculate the limiting potential for a copper deposition it was necessary only to specify the chloride ion concentration and the total residual copper after electrolysis and add 10 millivolts for concentration polarization. Reasonable variations in the concentration of chloride and in the total volume did not affect the limiting potential for carrying out a determination.

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